STUDIES ON PHASE TRANSFORMATIONS IN NiTi SHAPE MEMORY ALLOY

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STUDIES ON PHASE TRANSFORMATIONS IN NiTi SHAPE MEMORY ALLOY

Smart materials can sense and respond to the environment around them like temperature, stress, light, pH, electric field, magnetic field, etc. in a predictable and useful manner. Smart materials and systems open up new possibilities and can simplify devices and reduce weight with increased reliability. Smart materials include different classes of materials like piezoelectric, thermochromic, photochromic, magnetorheological materials, shape memory alloys etc. Study of the stability of these smart materials under service condition is a fundamental requirement before they can be used in applications.

Shape memory alloy (SMA) is one of the most important thermo-active smart materials. Shape memory refers to the ability of certain materials to "remember" their shape after severe deformations. Once deformed at low temperatures, these materials will stay deformed in that temperature and upon heating they spontaneously return to their original, pre-deformed shape [1]. Shape memory alloys undergo thermoelastic martensitic transformation which gives rise to the shape memory effect (SME) and pseudoelasticity (PE) [2]. The martensitic transformation is a diffusionless phase transformation in solids, where atoms move cooperatively, and often by a shear-like mechanism [3]. Martensite transformation can be initiated by cooling the material below M_s defined as the temperature at which the martensitic transformation begins. M_f is the temperature at which the martensitic transformation is completed. The martensitic transformation is reversible, with A_s as the temperatures at which the austenitic transformation (martensite $\rightarrow$ austenite) begins upon heating and the temperature at which the austenitic phase formation ends is designated as A_f [4]. SMAs may have two

different kinds of SMEs, commonly known as one-way shape memory effect (OWSME – remembers only high temperature shape) and two-way shape memory effect (TWSME – remembers shape of both low and high temperature phases).

Shape memory effect is associated with the thermoelastic martensitic transformation and reverse phase transformation. However, in reality, the process is not completely reversible. Irreversible processes are repeated during thermal cycling, causing a change in transformation characteristics [5]. Degradation of the material gets accelerated due to the phase transformation in every cycle [6,7].

The applications using SMA are very strongly dependent on the transformation temperature ranges of the alloys. Nitinol is a near equi-atomic intermetallic alloy consisting of Nickel (Ni) and Titanium (Ti). It was first prepared in the US Naval Ordinance Laboratory (NOL) in the year 1965, by Buehler and his associates [8].

NiTi and NiTi-based alloys have the best shape memory behavior among all shape memory alloys. They are generally ductile and can be deformed reasonably well. They have high strength, corrosion resistance, long fatigue life, stable configuration and elevated temperature stability giving rise to substantial advantages over Cu-based and Fe-based shape memory alloys [9]. In NiTi SMAs, the martensite phase has B19' structure and the austenite phase has B2 structure [10]. Further, an intermediate phase known as R-phase with rhombohedral structure may exist during B2↔B19' phase transformation under some special conditions [11]. The application of NiTi SMA in actuators is still limited due to the lack of cyclic stability of the material. Literature survey shows that the transformation characteristics and phase formation is very sensitive to composition, thermomechanical history and thermal cycling. Dislocation structure introduced during thermal cycling creates an anisotropic stress field which

helps the formation of preferentially oriented martensite variants, resulting in a macroscopic shape change during thermal transformation cycles.

The effect of deformation is important because it is predicted that defects such as dislocations introduced by plastic deformation influence the stability of each phase [12,13]. The width of the transformation is broadened by plastic deformation, and with subsequent annealing an intermediate phase is introduced. Effects of thermal cycling and annealing after deformation on the transformation of NiTi are attributed to transformation-induced defects like dislocations and it is inferred that the defects make it possible to stabilize the intermediate phase [13]. The role of R-phase in limiting the two-way memory effect is well known. Magnitude of the two-way memory depends on the formation of stress induced martensite or martensite reorientation during training procedure, the number of training cycles, the training stress and prior heat treatment [14].

Various techniques like differential scanning calorimetry (DSC), electrical resistivity measurements (ER), internal friction (IF), magnetic susceptibility measurements and thermomechanical analysis (TMA) have been commonly employed to study the transformation behavior of different shape memory alloys. X-ray diffraction (XRD) has been mainly used to characterize shape memory alloys as a supporting tool. The amount of information gathered from each technique varies, since some techniques reveal maximum information about phase transformation and some do not reveal as much information. Therefore, the technique used for characterizing the shape memory behavior has a unique significance.

Considerable amount of work has been carried out on the thermomechanical effects such as cold work, hot work, heat-treatment, mechanical cycling, thermal cycling

etc. Out of these thermomechanical variants, thermal cycling is most important during actuator design.

An actuator has to perform between two temperatures and has to undergo thermal cycling. Due to the introduction of dislocations in each cycle, the designed shape change required for a specific application may not be retained after several cycles. An actuator may be subjected to work at different thermal cycling rates, different cycling programmes and may be held at the high temperature phase for a long period during its operation or, mechanical operations like cutting and polishing may be performed while fabricating an actuator. All these factors may affect the transformation characteristics.

To the best of our knowledge, no systematic studies have been carried out on the effect of thermal cycling on the phase transformation behavior of Ti-rich NiTi SMA under actuation conditions. Therefore, studies on phase transformation characteristics of Ti-rich NiTi as a function of thermal cycling under various conditions have been taken up.

In the present work, an attempt is made to carry out the following studies

1. Phase evolution as a function of temperature during thermal cycling using X-ray diffraction analysis.
2. Effect of thermal cycling on mechanically cut and polished SMA.
3. Thermal cycling at different rates, in steps and holding at the high temperature phase for different periods.
4. Effect of thermal cycling on the dimensional stability of SMA.

During the study, the potential of each of the characterizing technique used in revealing information has been highlighted.

The thesis is divided into seven chapters. A brief description of the contents dealt in each chapter is given below.

A general introduction to 'shape memory effect' and 'shape memory alloys' along with 'thermoelastic martensitic transformation' is given in chapter 1. The mechanism of shape memory effect, and the phenomenological differences between one way and two way shape memory effect have been highlighted. Elements of thermodynamical theory of martensitic transformation and phase diagram of NiTi alloy system have been briefly discussed. The effect of composition on the phase transformation temperature is described. Review of literature relevant to the thermo-mechanical effect on NiTi alloy, motivation and objective of the present work have also been included in this chapter.

In chapter 2, details of the shape memory alloy used, method of heat-treatment given, procedure followed in thermal cycling and the experimental techniques employed are described. Ti-rich NiTi alloy in the form of sheet and wire, having identical thermal and mechanical history, have been selected for the study. The procedure followed in the heat treatment and thermal cycling rendered to the materials is described. Differential scanning calorimetry (DSC), electrical resistivity (ER), powder X-ray diffraction (XRD), thermomechanical analyzer (TMA), atomic force microscopy (AFM) and optical microscopy are used for the characterization of the SMA. The principle of operation of each of the technique used is briefly described.

Results of the investigations on the effect of thermal cycling on the transformation behavior of Ti-rich NiTi SMA sheet heat treated at 660 °C, by analyzing the changes in powder XRD patterns recorded at various temperatures, are presented in chapter 3. X-ray diffraction studies as a function of specimen temperature would yield information on the evolution of a particular phase with temperature. Powder XRD data

were recorded in the range +25 °C to +160 °C at an interval of 10 °C, during heating and cooling. DSC was carried out on the specimen in the same temperature range at a scanning rate of 10 °C/min., for comparison. The thermal hysteresis width corresponding to the M↔A phase transformation, observed through XRD, is large when compared to that measured from DSC. Powder XRD study seems to be more sensitive as it can detect even minute amounts of a particular phase compared to DSC, which can only reveal the behavior of major phase. Thermal cycling on SMA is carried out by immersing the samples successively for two minutes each in liquid paraffin baths maintained at +160 °C and room temperature (RT). During the initial few thermal cycles A_s and A_f decrease, after which they remain fairly constant, whereas M_s and M_f do not change significantly due to thermal cycling, as observed from the temperature dependent XRD studies. It should be noted that the observed change in M_s and M_f are less than 10 °C and the XRD patterns were recorded at an interval of 10 °C. Integrated area under the austenitic peak increases rapidly with the number of thermal cycling up to N = 5 and continues to increase even up to N = 50. The initial large increase in the integrated peak area with thermal cycling (up to N = 5) is attributed to the increased austenitic phase, whereas at larger number of cycles, the increase may be due to a better orientation of austenite grains, as indicated by the change in latent heats observed through DSC.

Presence of an oxide layer affects the transformation behaviors of SMAs and to avoid these effects the oxide layer needs to be removed. The approach adopted for removing the oxide layer may be of significance from thermomechanical considerations. Further, SMA sheets or wires need to be cut into precise size and shape, for any particular application. Chapter 4 presents the results of the studies on the effect of mechanical work such as mechanical cutting and polishing on the shape memory

transformation behavior of Ti-rich NiTi alloy heat treated at 560 °C (HT560MC) and 660 °C (HT660MC). The results are compared with those of the samples heat treated after cutting followed by chemical etching to remove the oxide layer (HT560CE and HT660CE). The samples were subjected to thermal cycling using paraffin bath and were characterized using DSC, ER and XRD techniques. DSC was carried out on the samples in the temperature range from RT to +160 ^{o}C at a scanning rate of 3 ^{o}C/min. The electrical resistivity as a function of temperature was measured using a home made four probe measurement setup in the same temperature range. XRD data were recorded in the range +25 °C to +160 °C at an interval of 10 ^{o}C, in general, and at intervals of 5 ^{o}C near the transformation temperatures.

Mechanically cut and polished samples show broad thermal width, lesser heat flow, lower X-ray peak intensity, larger FWHM, lesser ER shift of martensite due to cycling over chemically etched samples. In other words, the chemically polished sample shows rapid and strong phase transformation whereas the mechanically polished sample undergoes slow and diffuse phase transformation, due to the internal stresses and increased dislocation density. Mechanically polished samples show more stability in transformation characteristics with regard to thermal cycling compared to chemically etched samples. The dislocations and stress generated by the mechanical cutting and polishing may be responsible for the absence of R-phase peak due overlapping of phases in HT560MC and HT660MC samples, subjected to thermal cycling during reverse transformation. Both samples heat treated at 560 ^{o}C and 660 ^{o}C, show the effect of mechanical cutting and polishing even at the 150th thermal cycling. Heat treatment at a higher temperature shows more stability in phase transformations characteristics. ER and XRD seem to be more sensitive compared to DSC in detecting R-phase. XRD can provide evidence for the presence of R-phase in samples even at very low fraction of

that phase. Use of more than one characterizing technique gives more information about the phase transformation in SMAs.

In chapter 5, the effect of scanning rate, step heating/step cooling and aging at a temperature above A_f or austenite aging on the phase transformation behavior of Ti-rich NiTi SMA using DSC is dealt. Investigations have been carried out on Ti -rich NiTi SMA sheet heat treated at 560 °C. DSC was carried out on the specimen in the temperature range from RT to +160 ^oC at scanning rates of 0.5, 3 and 25 ^oC/min., under nitrogen atmosphere and also with different cycling schemes like step heating and austenitic aging, for different periods of time. Rapid thermal cycling was carried by immersing the sample in paraffin bath at two temperatures successively, for comparison. Studies on the thermal cycling at different rates indicate that stabilization of the martensite takes place at a slow rate, by means of self accommodation of phases with respect to each other. Rapid thermal cycled sample shows R-phase separation to a large extent indicating increased density of dislocations due to rapid heating and cooling cycles. Higher heating/cooling rate is preferred for large transformation strain and slow heating/cooling rate is recommended for narrow temperature range actuators. During stepwise thermal cycling, sample was heated/cooled at ~3 ^oC/min. and after every 10 ^oC increase /decrease, sample was held at that temperature for 15 minute with the help of a DSC program. In the case of step thermal cycling, due to partial annealing of defects introduced by thermal cycling, appearance of R-phase gets shifted to higher number of cycles. In addition to this, the step thermal cycled sample shows higher heat flow during phase transformation compared to continuous cycling.

Low temperature aging study was carried out on the specimen subjected to a cycle in the temperature range from RT to +160 ^oC at scanning rate of 3 ^oC/min. under nitrogen atmosphere. In every cycle, the sample was maintained at +160 ^oC, for

different periods of time (0, 1, 5, 10 and 20 hours) before cooling to room temperature using DSC program. Samples with 0 and 1 hour of aging show R-phase, increased thermal width and reduced enthalpy of transformation. Stabilization of martensitic transformation is observed for 10 and 20 hours of aging. Annihilation of defects introduced by the thermal cycling may be responsible for the reduced growth of R-phase, less thermal width and larger enthalpy of transformation with an increase in the period of aging. Aging of austenitic phase results in the stabilization of transformation temperatures.

The studies on the dimensional stability of Ti-rich NiTi SMA under thermal cycling is discussed in chapter 6. Ti-rich NiTi alloy samples in the form of a wire of 0.787 mm diameter were heat treated at two different temperatures (560 °C and 660 °C). The dilatometric measurements were carried out using elongation mode of TMA in the range of RT to +160 °C and subjected to thermal cycling using TMA temperature program. Phase transformation temperatures and presence of different phases observed in TMA are compared with DSC results. Permanent dimensional change is observed as a result of thermal cycling. Another important observation is that the thermal expansion coefficient changes its sign as a result of R-phase formation. TMA plots of samples heat treated at 560 °C and 660 °C are slightly different and this may be due to the difference in the extent of R-phase present, as heat treatment at higher temperature reduces dislocations and thereby, the R-phase to a lower extent. At a higher number of thermal cycling, martensitic phase shows more dimensional stability compared to austenitic phase. Results indicate that TMA can distinguish overlapped phase transformation while DSC cannot distinguish such a transformation.

The major conclusions drawn from the present studies are summarized in chapter 7.

References:

[1]. Wayman C M and Duerig T W, "*Engineering Aspect of Shape Memory Alloys*", Edited by Duerig T W, Melton K N, Stokel D and Wayman C M, Butterworth-Heinemann Ltd., England, 1990, p.3.

[2]. Tobushi H, Iwanaga H, Ohashi Y, Inaba A, Kawaguchi M and Saida H, *JSME Int. Journal* **33** (1990) 256.

[3]. Otsuka K and Wayman C M, "*Shape Memory Materials*", Edited by Otsuka K and Wayman C M, Cambridge University Press, 1998, p.3.

[4]. Gil F J, Manero J M and Planell J A, *J. Mater. Sci*. **30** (1995) 2526.

[5]. Miyazaki S, IgoY and Otsuka K, *Acta metall*. **34** (1986) 2045.

[6]. Turenne S, Prokoshkin S, Brailovski V and Sacepe N, *Canadian Metallurgical Quarterly* **39** (2000) 217.

[7]. Kwarciak J, Lekston Z and Morawiec H, *J. Mater. Sci*. **22** (1987) 2341.

[8]. Buehler W J, Gilfrich J V and Wiley R C, *J. Appl. Phys*. **34** (1963) 1475.

[9]. Xu H, Jiang C, Gong S and Feng G, *Mater. Sci. Eng. A* **281** (2000) 234.

[10]. Kudoh Y, Tokonami M, Miyazaki S and Otsuka K, *Acta metall.* **33** (1985) 2049.

[11]. Wang F E, De Savage B F, Buehler W J and Holster W R, *J. Appl. Phy.* **39** (1968) 2166.

[12]. Miller D A and Lagoudas D C, *Mater. Sci. Eng. A* **308** (2001) 161.

[13]. Matsumoto H, *Phys. B.* **190** (1993) 115.

[14]. Liu Y and McCormick P G, *Acta. Metall. Mater.* **38** (1990) 1321.

List of Research Papers Published in Journal /Conference

1) Effect of thermal cycling on the shape memory transformation behavior of NiTi alloy: Powder x - ray diffraction study
   Manjunatha Pattabi, **K. Ramakrishna** and Mahesh.K. K
   Materials Science & Engineering A **448** (2007) 33.

2) Effect of mechanical cutting and polishing on the shape memory transformation behavior of NiTi alloy
   Manjunatha Pattabi and **K. Ramakrishna**
   Materials Science & Engineering A **486** (2008) 14.

3) Effect of Low Temperature Aging on the Phase Transformation Behavior of NiTi Shape Memory Alloy
   K. Ramakrishna and Manjunatha Pattabi
   International Conference on Recent Trends in Materials and Characterization RETMAC 2010, February 14-15, 2010.
   National Institute of Technology, Suratkal, Karnataka.

4) Effect of Thermal Cycling at Different Rates on Phase Transformation Behaviors of NiTi Shape Memory Alloy
   K. Ramakrishna and Manjunatha Pattabi
   AIP Conference Proceedings **1349** (2011) 145.

Book Chapters:

- Phase Transformation in NiTi Shape Memory Alloy under Thermomechanical Conditions
  Manjunatha Pattabi and **K. Ramakrishna** in "Shape Memory Alloys: Manufacture, Properties and Applications" (Ed) H. R. Chen, Chapter 11, pp. 317-338 (Nova Science Publishers, New York, 2010), ISBN: 978-1-60741-789-7

- Phase Transformation in NiTi Shape Memory Alloy under Thermomechanical Conditions
  Manjunatha Pattabi and **K. Ramakrishna** in "Encyclopedia of Materials Science Research (2 Volume Set)" (Ed) Batukhan B. Chinbat and Sora H. Mori, (Nova Science Publishers, New York, In Press), ISBN: 978-1-61209-954-5

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